



12th International Conference on Muon Spin Rotation, Relaxation and Resonance

Depth-dependent spin dynamics in TbMnO₃ thin films measured by low energy muon spin relaxation

Matthias Bator^{a*}, Yi Hu^a, Hubertus Luetkens^{b*}, Christof Niedermayer^b, Thomas Prokscha^b, Andreas Suter^b, Zaher Salman^b, Michel Kenzelmann^b, Christof W. Schneider^a, and Thomas Lippert^a

^aPaul Scherrer Institute, Department General Energy, Villigen PSI, Switzerland

^bPaul Scherrer Institute, Department Research with Neutrons and Muons, Villigen PSI, Switzerland

Abstract

We report on low energy muon measurements performed on 100 nm and 28 nm thin epitaxial, highly strained and twin free TbMnO₃ films grown on (110) YAlO₃ substrates by pulsed laser deposition ($\lambda = 248\text{nm}$, $\nu = 2\text{ Hz}$, $T_S = 760^\circ\text{C}$). These investigations were done at the LEM beamline at the PSI, Switzerland which allowed for depth-dependent analysis of the muon spin relaxation rate as a function of temperature. A clear decrease of the relaxation rates could be observed in regions near the substrate/thin film interface compared to measurements at the surface or in the middle of the films. This behavior could be attributed to a strain-induced change of the Tb spin dynamics. Furthermore, it could be shown that the films are fully magnetic below a temperature of 40 – 50 K, which agrees well with susceptibility measurements performed on these films as well as with the bulk literature value of $T_{N,Mn} = 41\text{ K}$.

Keywords: Multiferroic; spin dynamics; rare-earth manganate; low energy μSR ;

1. Introduction

Multiferroics (MF), materials with two or more ferroic properties – ferroelectricity (FE), ferromagnetism (FM), ferroelasticity – [1] in the same phase are known for a long time [2] but only recently gained a lot of interest due to novel materials with improved MF properties [3]. The orthorhombic rare earth manganates (o-ReMnO₃), crystallizing in the perovskite crystal structure are particularly interesting due to their relatively high induced polarization and strong magnetoelectric (ME) coupling. It was shown that this is caused by a magnetic inversion symmetry breaking and a subsequent reorganization of the oxygen octahedral around the Re⁺ ions [4,5]. Therefore, the Re⁺ ion-size has a large influence on the actual ME transition mechanism.

The Re⁺ ion-size further determines the crystal structure (hexagonal for small ions: Ho, Er, Tm, Lu; orthorhombic for larger ions: Gd, Tb, Dy), rendering it impossible to grow large volume orthorhombic

* Corresponding authors. Tel.: +41 (0)56 310 4732; fax: +41 (0)56 310 2688.

E-mail address: matthias.bator@psi.ch; hubertus.luetkens@psi.ch

bulk single crystals for the above mentioned Re. This can be overcome by growing epitaxial thin films where the crystal structure can be defined by the growth conditions and choice of substrate material. The substrate material defines the kind of strain as well as its strength thus probably also influencing the final material properties like the ME transition mechanism, polarization strength and transition temperature. Due to relaxation of the strain throughout the thin film differences of the film properties at the surface, the center of the film and at the substrate/film interface are expected. Typical relaxation lengths of strain in a thin film are on the scale of a few ten nm. It was shown that the strain in a thin film typically relaxes fully after $\sim 60 - 80$ nm depending on the growth parameters [6].

2. Sample preparation and experimental techniques

The TbMnO_3 thin films investigated were grown by pulsed laser deposition (PLD). A pressed and sintered stoichiometric TbMnO_3 cylinder was used as target. The laser ablation was performed using a KrF excimer laser with a wavelength of $\lambda = 248$ nm, operated at $\nu = 2$ Hz repetition rate. (110) YAlO_3 substrates were used for epitaxial growth. The substrate unit cell parameters of $a = 5.12$ Å, $b = 5.29$ Å, $c = 7.31$ Å are very similar to those of TbMnO_3 with $a = 5.3$ Å, $b = 5.86$ Å and $c = 7.49$ Å resulting in strained growth. The substrate was heated to 760°C and the deposition was performed in 2×10^{-1} mbar O_2 background pressure. An additional N_2O gas pulse synchronized to the laser pulse was used to increase the amount of O^- ions created in the plasma while removing possible bigger particles in the plasma. The measured overall pressure including the gas pulse was 2.2×10^{-1} mbar. The films were grown with 9000 and 2400 pulses resulting in thicknesses of ~ 100 nm and ~ 28 nm, respectively. Films with different strains (results not shown here) were achieved by growing on different substrates including (100), (110) SrTiO_3 or (110) NdGaO_3 . These substrates are chosen due to their unit cell parameters to guarantee an epitaxial growth of the thin films. The typical roughness values for the substrates are $R_a < 0.25$ nm and $R_{p,v} < 3.0$ nm.

Structural characterization was made by $\theta - 2\theta$ scans in x-ray diffraction to determine the crystalline quality (see Fig. 1). Phase pure growth could be confirmed for both films with good crystallinity, the FWHM is 0.06° , and at the resolution of the diffractometer.

Muon spin relaxation measurements were performed at the low-energy muon (LEM) beamline of the PSI, Switzerland [7]. There, the muon energy is tunable in the range of $0 - 30$ keV thus allowing muon implantation in thin films at specific depths. Monte-Carlo calculations were performed to determine the implantation depth and a set of energies for both films was chosen to cover a wide range of distances between measured region and substrate/film interface (SFI).

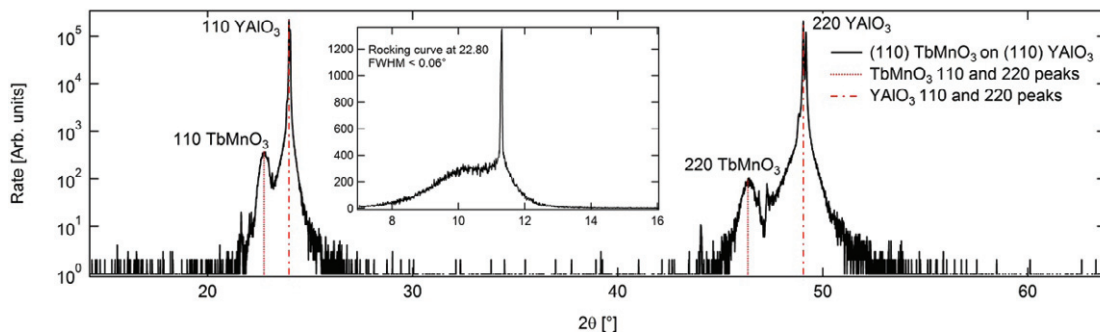


Fig.1. $2\theta - \theta$ scans of an (110) oriented TbMnO_3 thin film grown on 110 YAlO_3 . The inset shows a rocking curve of the 110 TbMnO_3 peak with a FWHM of 0.06° . Small additional feature in front of the 110 and 220 TbMnO_3 peaks are instrumental artefacts.

The films were mounted on Ag as well as on Ni sample holders. The very fast relaxation of the muon spin ensemble in Ni allowed for an evaluation of the ratio of magnetic to non-magnetic fraction of the film, taking into account the known sizes for thin film and uncovered substrate area as well as the known total asymmetry of the system.

The measurements were performed in a temperature range of 5 – 250 K covering both transitions at $T_{N,Mn^{3+}} = 41$ K, the ordering temperature of Mn^{3+} spins and $T_{lock-in} = 28$ K, the so-called lock-in temperature where the spins reorder and induce a ferroelectric polarization.

3. Results and Discussion

The signal for the $TbMnO_3$ was fitted by a single exponentially damped cosine function. Weak transverse field measurements were used to discriminate the signal fractions originating from the Ag backing plate (visible at small temperatures) and the $TbMnO_3$. It also makes the measurement insensitive to the small increase of the beamspot which is usually observed at low muon implantation energies.

A temperature scan between 250 K and 5 K disclosed a continuous increase of the muon spin relaxation rates already below 250 K; see the weak transverse field (50 G) μ SR spectra in Fig. 2. These relaxation rates can reach very high values for low temperatures and are at the limit of the system resolution. Furthermore, an overlap with the signal from the Ni holder happens at low temperatures. Therefore, several fitting steps were performed. High temperature measurements were used to determine the temperature-independent fraction of the very fast Ni signal. A remaining weakly relaxing low energy μ SR signal at low temperatures can be fully attributed to muons being stopped in the non-magnetic $YAlO_3$. Comparing this signal to the total area of the beam and to the area of the $TbMnO_3$ film as well as considering the known total asymmetry for the system, allows to conclude that the measured thin film volume is fully magnetic below 40 - 50 K. This agrees well with the literature bulk value for antiferromagnetic ordering of the Mn^{3+} spins at $T_{N,Mn^{3+}} = 41$ K.

The transition temperature of the Mn spin system is not very sharp due to a steady increase of the relaxation rate already well above $T_{N,Mn^{3+}} = 41$ K. This can be attributed to the presence of the large Tb^{3+} spin moments. Although the Tb spin ordering temperature is as low as $T_{N,Tb^{3+}} = 4$ K, a gradual slowing down of the Tb spin fluctuations is already visible below 250 K [8]. Later measurements confirmed that the observed muon spin relaxation is mainly caused by the Tb spins by measurements on a $ReMnO_3$ thin film with a non-magnetic Re (results not shown here).

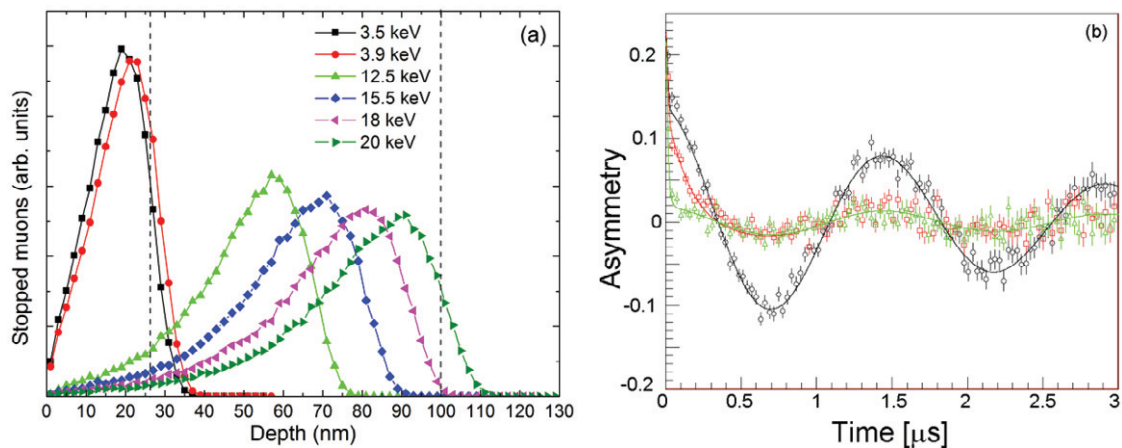


Fig. 2. (a) Muon stopping profiles from Monte-Carlo calculations. Dashed lines indicate the film thicknesses used in the experiments. (b) Asymmetries of $TbMnO_3$, partly exposed $YAlO_3$ substrate and Ni from the holder for different temperatures (black: 250K, red: 75K, green: 5K) on a timescale of 0 to 3 μ s.

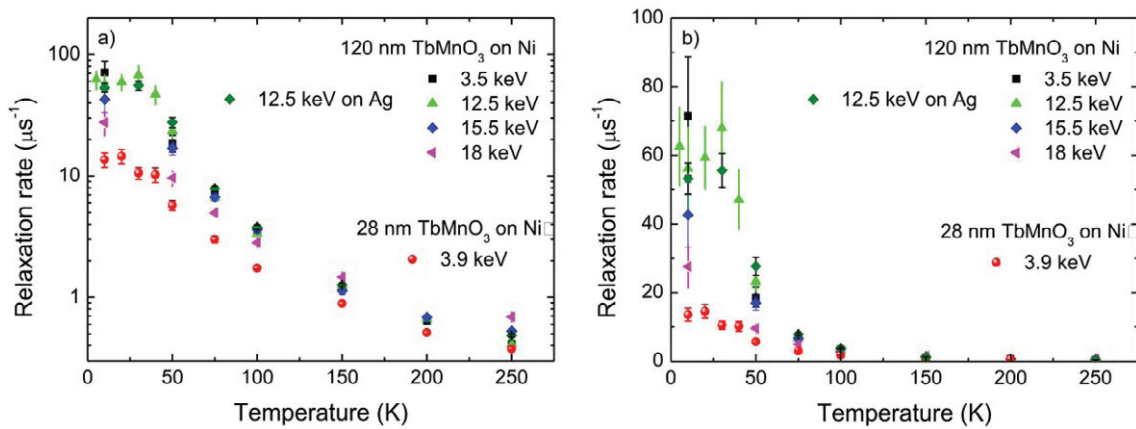


Fig. 3: Relaxation rates dependent on temperature and muon implantation depth on a) a linear and b) logarithmic scale for the 100 nm thin TbMnO_3 film on Ni and Ag and for the 28 nm TbMnO_3 film on Ag. The continuous increase caused by the Tb^{3+} spins below 250 K is clearly visible on the log scale. The trend to lower relaxation rates towards the SFI can be observed.

The possibility to tune the muon implantation energy was used to implant muons at different depths in the TbMnO_3 thin film. The energies used, 3.5 keV, 12.5 keV, 15.5 keV and 18 keV, correspond to implantation distances of 82, 44, 30 and 13 nm, respectively, to the substrate/film interface. A strong decrease of the spin relaxation can be observed across the whole temperature range for measurements towards the SFI. Starting from the surface towards the SFI at 10 K the relaxation rates change from $71 \pm 17 \mu\text{s}^{-1}$ to 58 ± 12 to $42 \pm 10 \mu\text{s}^{-1}$ and finally to $27 \pm 6 \mu\text{s}^{-1}$, a significant decrease of 60% (see Fig. 3). This behavior is probably caused by the change in the strain through the film which is strongest directly at the interface and decreases fast towards the surface resulting in increasing spin relaxation. A similar depth-dependent decrease of the spin dynamics was already observed in AuFe and CuMn spin glasses by Morenzoni *et al.* [9]. However in this case, the spin dynamics increases towards the surface of the films.

In order to increase the resolution of the low temperature relaxation rates and confirm the results further measurements were performed with samples mounted on a Ag holder. To check comparability the same 100 nm TbMnO_3 thin film was re-measured with an implantation energy of 12.5 keV. The results agree perfectly with those obtained on Ni.

A ~ 28 nm thin 8×10 mm² TbMnO_3 film without exposed YAlO_3 substrate area was measured with a muon implantation depth of ~ 6 nm above the SFI. In this case some of the muons reached the substrate below the thin film. Their contribution was accounted for together with the muons deposited in the Ag holder as both materials show a similarly slow relaxation. The measured relaxation rate of $13 \pm 1.5 \text{ s}^{-1}$ agrees well with the expectations raised by the previous measurements on the 100 nm thin film. The trend to lower relaxation rates towards the SFI remains.

The change in relaxation rates towards the SFI can be caused by different effects. For one the spin dynamics could change as a result of the differences in strain. It is known, that the Mn-O-Mn octahedra can be tilted as a result from different *Re* ion sizes or as the result from an external force like stress [10]. Another observation made in polarized neutron reflectometry measurements (results not shown here) suggests a change in the Mn magnetism as an effect of the strain in the film at the SFI, which would indirectly cause a change of the Tb spin dynamics. Due to the generally high relaxation rates and the already fully magnetic films the multiferroic transition at $T_{\text{lock-in}} = 28$ K could not be observed.

4. Conclusion and Outlook

We were able to show that TbMnO_3 thin films are fully magnetic below 40-50 K. A continuous increase of the muon spin relaxation rate below 250 K was observed and could be associated with the slowing down of Tb^{3+} spins. Measurements with different muon implantation depths have shown a strong trend of decreasing relaxation times towards the substrate/film interface. The most probable explanation for this is a change in strain and its influence on the local magnetism in the film which is the strongest directly at the interface and relaxes towards the surface. Further neutron and muon measurements supporting this assumption have been performed recently and results will be reported elsewhere.

Future experiments will be performed on different ReMnO_3 thin films including Re without a magnetic moment. The aim will be to gather data with better statistics in the temperature region of 20 – 50 K as well as to further investigate the Mn spin dynamics in the absence of the Re moment directly at the substrate/film interface.

Acknowledgements

This work was partially supported by SNF, Project No. 200020-117642, MaNEP, and the Paul Scherrer Institute. We also gratefully acknowledge fruitful discussions with J. White. Part of this work was performed at the Swiss Muon Source ($\text{S}\mu\text{S}$), Paul Scherrer Institute (PSI, Switzerland).

References

- [1] H. Schmid, Multi-ferroic magnetoelectrics, *Ferroelectrics* 162 (1994) 317-338
- [2] V.G. Bar'yakhtar and I.E. Chupis, Phenomenological Theory of the ferroelectric magnet, *Sov. Phys. Solid State* 10, (1969) 2818-2821
- [3] Nicola A. Spaldin and Manfred Fiebig, The renaissance of magnetoelectric multiferroics, *Science* 309, (2005) 391-392
- [4] M. Kenzelmann, et al., Magnetic Inversion Symmetry Breaking and Ferroelectricity in TbMnO_3 , *Phys. Rev. Lett.* 95, (2005) 087206
- [5] V. Pomjakushin, M. Kenzelmann, et al., Evidence for large electric polarization from collinear magnetism in TmMnO_3 , *New Journal of Physics* 11, (2009) 043019
- [6] C.J.M. Daumont, et al., Epitaxial TbMnO_3 thin films on SrTiO_3 substrates: a structural study, *J. Phys.: Condens. Matter* 21 (2009) 182001
- [7] T. Prokscha, E. Morenzoni, K. Deiters, F. Foroughi, D. George, R. Kobler, A. Suter, V. Vrankovic, The new μE4 beam at PSI: a hybrid-type large acceptance channel for the generation of a high intensity surface-muon beam, *Nucl. Instr. Meth. A* 595 (2008) 317
- [8] A. A. Nugroho, et al., Changes of spin dynamics in multiferroic $\text{Tb}_{1-x}\text{Ca}_x\text{MnO}_3$, *Physica B* 404 (2009) 785
- [9] E. Morenzoni, et al., Depth-Dependent Spin Dynamics of Canonical Spin-Glass Films: A Low-Energy Muon-Spin-Rotation Study, *Phys. Rev. Lett.* 100, (2008) 147205
- [10] T. Goto, et al., Ferroelectricity and Giant Magnetocapacitance in Perovskite Rare-Earth Manganites, *Phys. Rev. Lett.* 92 No. 25 (2004) 257201